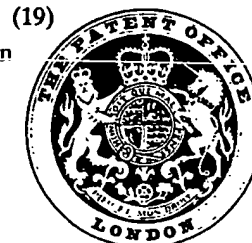


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(54) CARRIER GRANULES FOR NONIONIC DETERGENTS

(71) We, THE PROCTOR & GAMBLE COMPANY, a corporation organised and existing under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:-

This invention relates to spray-dried carrier granules suitable for holding an organic detergent, and to their production. More particularly, it is concerned with the production of spray-dried carrier granules which have a bulk density controlled within a certain range and which are suitable for holding an organic nonionic detergent.

The term "carrier granules" is used herein to denote granules which can absorb, or otherwise hold, a substantial proportion of a liquid or low melting material, without acquiring stickiness or other objectionable properties, and without easily releasing the absorbed material on to or into contiguous surfaces.

Detergent compositions for the cleaning of soiled laundry are generally referred to as "heavy duty" or "built" detergent compositions. Typically, they contain a soap or an organic synthetic detergent, and a builder for sequestering or otherwise removing hardness producing ions which are liable to be found in the water of the region in which they are to be used; they may optionally contain various other components, e.g. alkali metal silicates, sodium sulphate, or bleaches. Most built detergent compositions are produced in a solid granular form. A

process well-known in the detergent industry for producing these granular built detergent compositions comprises forming an aqueous slurry of most if not all of the desired components, and thereafter spray-drying the slurry to form granules.

Built detergent compositions which at present are in widespread use generally contain a water-soluble organic anionic detergent as the principal soil-removing component. These detergent compositions have utility in removing a wide range of stains. Their ability to remove grease and oil stains, however, is more limited than might be desired, this point being especially apparent when polyester fabrics carrying greasy and oily stains are laundered in aqueous laundry baths.

Organic nonionic detergents are known to be especially effective in removing greasy and oily stains, but despite this property the use of these nonionic detergents as a major soil-removing agent in commercial detergent compositions has so far not been substantial. Various drawbacks affecting processing and performance have hindered the introduction of a nonionic detergent based composition. For example, certain organic nonionic detergents incorporate relatively volatile components with the result that, when aqueous slurries containing these components in significant proportions are spray-dried, they contribute fumes to the spray-drier exhaust gases to such a degree that it would be objectionable to discharge these gases directly into the atmosphere.

Various processing techniques have been tried for solving the problems arising from the inclusion of a nonionic detergent in a

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detergent composition. One processing technique which has received considerable attention is that using carrier granules, as herein defined, to absorb or otherwise hold the nonionic detergent. Thus a variety of carrier granules have been suggested as being suitable for carrying an organic nonionic detergent sprayed on to them. The incorporation of the nonionic detergent in the detergent composition by means of the carrier granule technique does avoid the need to include the nonionic detergent in the aqueous slurry which is to be spray-dried, thus eliminating the fume emission problem, but unfortunately certain other drawbacks are encountered. In the first place, even when a nonionic detergent loaded carrier has been prepared, it has still to be mixed with other detergent composition components, so that the number of processing steps is increased. Also, the various carriers that have been suggested may themselves constitute an undesirable load in the detergent composition, in the sense that, although the carrier performs the necessary function of enabling the nonionic detergent to be incorporated in the composition, in many instances it does not itself function as a soil-removing agent.

It would be desirable to produce carrier granules composed of various desired components of a spray-dried detergent composition. If it were possible to spray-dry an aqueous slurry containing the desired components of a detergent composition, other than the detergent, thus producing what may be called a detergent composition matrix, and thereafter to spray the nonionic detergent on to the spray-dried matrix, the above-mentioned problems would be solved. Unfortunately, producing a satisfactory spray-dried carrier matrix has proved difficult, in that the density of the spray-dried granules has been undesirably high. Furthermore, since the granules must afterwards be sprayed with a nonionic detergent, the density of the final loaded granules has been even more undesirably high.

A relatively low and uniform density is preferred by the housewife. Moreover, careful control of the density of spray-dried detergent composition granules is necessary for the following reasons: (1) usage instructions normally advise the user to employ a certain volume of a product; (2) a segregation problem may arise if components of a different density are dry-mixed with the spray-dried composition; and (3) most package filling machines meter the product, by volume, into standard sized containers which are required to contain a controlled weight of product.

It has now been found that the addition of one or more phosphate esters, as hereinafter specified, to an aqueous slurry of a substan-

tially organic detergent free composition before spray-drying has a valuable effect on the density of the resultant spray-dried granules. The resultant spray-dried granules have in fact a low density and are suitable as carrier granules on to which a nonionic detergent is sprayed.

According to the present invention, we provide carrier granules, as herein defined, having a bulk density of from 300 grams/litre to 500 grams/litre, the granules being produced by a spray-drying operation, being suitable for holding an organic nonionic detergent, and consisting essentially of (by weight):

(a) from 30% to 70% of a water-soluble alkaline inorganic builder salt;

(b) from 2% to 10% of an alkali metal silicate having a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of from 3.2:1 to 1:1;

(c) from 10% to 50% of an alkali metal sulphate; and

(d) from 0.05% to 1.5% of one or more phosphate esters having the formula $(\text{RO})_2(\text{PO})(\text{OX})$ wherein X is H, alkali metal, ammonium or substituted ammonium, and R is H or $\text{R}_1(\text{OC}_2\text{H}_4)_n\text{OH}$ wherein n is 0 to 30 and R_1 is an unbranched or branched alkyl or alkenyl group containing from 8 to 22 carbon atoms when n is 0 and containing from 2 to 22 carbon atoms when n is from 1 to 30, provided that no more than one R is H.

All percentages and ratios mentioned herein are by weight unless otherwise stated.

The carrier granules of the present invention can be produced by forming an aqueous slurry consisting essentially of water together with the above-mentioned ingredients "(a)", "(b)", "(c)" and "(d)", and spray-drying the slurry to form the carrier granules. The spray-drying of aqueous slurries is well-known, and may for example comprise atomising the afore said aqueous slurry having a temperature of from 40°C to 100°C, into the top of a spray-drying tower. In one spray-drying technique, hot air having a temperature of from 180°C to 380°C is introduced at the base of the tower. As the hot air rises, it contacts the atomized aqueous slurry droplets, thereby driving off some or all of the free water. The resultant granules are collected at the base of the tower, and the water-laden air passes out at the top. In another spray-drying technique, the hot air is introduced together with the atomized aqueous slurry droplets at the same end of the tower. An inert gas may be introduced into the aqueous slurry with a view to decreasing the density of the granules formed. These known spray-drying techniques may all be employed within the scope of the present invention as hereinafter described.

The phosphate esters of the formula

(RO), (PO) (OX) include mono- and dialkyl, mono- and dialkenyl, ethoxylated mono- and dialkyl, and ethoxylated mono- and dialkenyl acid phosphates, and alkali metal salts of these esters, including their sodium, potassium, ammonium and substituted ammonium salts.

Commercially available forms of the phosphate esters of the said formula may contain small proportions of condensed phosphates, and more particularly of pyrophosphates, polyphosphates and mono- and dialkyl ortho-phosphates. Minor amounts (e.g. up to 5% by weight) of trialkyl phosphate esters may also be present, having been produced during the preparation of the mono- and dialkyl phosphate esters.

Typical alkyl acid phosphates suitable for use in the granules of this invention are mono- or dipalmityl acid phosphate, distearyl acid phosphate, and the mono- or disodium salts thereof; alkenyl acid phosphates and their salts can also be used, e.g. dioleyl acid phosphate.

The alkyl acid phosphates can be prepared by reacting a phosphoric acid with a primary aliphatic alcohol having from 8 to 22 carbon atoms, preferably 12 to 18 carbon atoms. Procedures for performing these reactions are well-known in the art. Similarly, unsaturated aliphatic alcohols having these numbers of carbon atoms, e.g. oleyl alcohol, can be reacted with a phosphoric acid to produce an alkenyl acid phosphate. Secondary saturated or unsaturated aliphatic alcohols with the required number of carbon atoms can be reacted with a phosphoric acid to produce branched chain phosphate esters.

Ethoxylated alkyl or alkenyl acid phosphates can be prepared by phosphating compounds having the formula $R_1((OC_2H_4)_n OH)$ wherein R_1 contains from 2 to 22 carbon atoms, preferably 12 to 16 carbon atoms, and n is from 1 to 30, preferably 1 to 10. Examples of these phosphates are the addition products obtainable from: coconut fatty alcohol and 6 to 10 moles of ethylene oxide; oleyl alcohol and 10 to 20 moles of ethylene oxide; and stearyl alcohol and 10 to 30 moles of ethylene oxide. Preferably each R_1 of the phosphate ester is $R_1(OC_2H_4)_n OH$.

Examples of phosphating agents which can be used in preparing the phosphate esters are polyphosphoric acid and orthophosphoric acid. Other phosphating agents and mixtures of phosphating agents may be used if desired. U.K. Patent Specification No. 1,159,643 describes processes which may be employed for making the phosphate esters required for the granules of the present invention.

The desired phosphate ester(s), as indi-

cated earlier, will be included in an aqueous slurry from which the present granules are to be formed in a proportion of from 0.05% to 1.5%, preferably from 0.25% to 0.6% by weight, referred to the weight of the granules. A proportion of phosphate ester below 0.05% has no significant effect on the density of the granules. A proportion greater than 1.5% has no useful effect, i.e. produces no additional or further decrease in the density of the granules, and for this reason, is avoided.

The proportion of the alkaline inorganic detergency builder employed, as indicated earlier, is from 30% to 70% by weight, referred to the weight of the granules. Preferably this proportion is from 40% to 65%. Examples of suitable water-soluble, inorganic alkaline detergency builder salts useful in the granules of this invention are the alkali metal carbonates, phosphates, polyphosphates and bicarbonates. Specific examples of these salts are sodium and potassium bicarbonate, carbonate, tripolyphosphate and pyrophosphate. An especially preferred detergency builder is sodium tripolyphosphate.

Alkali metal silicate having a $SiO_2:M_2O$ ratio of from 3.2: 1 to 1: 1, preferably 1.5: 1 to 2.5: 1, is employed in a proportion of from 2% to 10% by weight, referred to the weight of the granules; preferably this proportion is 3% to 7%. An especially preferred alkali metal silicate is sodium silicate.

From 10% to 50%, preferably 12% to 40%, by weight, referred to the weight of the granules, of an alkali metal sulphate is employed in the granules of this invention. The sulphate may for example be sodium sulphate or potassium sulphate.

The balance of a slurry from which the present granules are to be formed comprises water. The proportion of water which it is advisable to employ in the slurry will depend in the first place upon what proportion is needed to produce a slurry having a viscosity low enough to facilitate or at least permit pumping and atomizing. Preferably the minimum proportion of water is used, so as to minimise the proportion of water which has to be removed later, and so as to minimise the cost of this subsequent water removal, provided always that enough water is used to provide a slurry that can be pumped and atomized. Generally, the slurry may contain from 25% to 60% of water.

Optionally, a variety of auxiliary detergent composition components may be included in the slurry. For example, suds suppressors, brighteners, dyes, anti-flocculating agents and soil-suspending agents may be added in minor proportions. These auxiliary components may also be dry-mixed with the loaded spray-dried granules as discussed hereinafter.

Minor proportions, e.g. below 5% by weight referred to the weight of the granules, of organic detergents can be included in the aqueous slurry without departing from the scope of this invention. Preferably, however, the slurry is detergent-free, so that fume emission problems (such as are encountered with certain nonionic detergents) can be avoided, and so that no other organic detergent is present to dilute the soil-removal performance of the nonionic detergent.

The aqueous slurry is spray-dried by any of the applicable procedures to produce the carrier granules of this invention, which generally contain less than 15% water, and which preferably contain 5% to 15% water.

The present spray-dried carrier granules have a bulk density of from 300 grams/litre to 500 grams/litre, preferably 350 grams/litre to 450 grams/litre. Density values at the lower end of these ranges can be achieved with the aid of an inert gas injection step. Gas injection is commonly used in the spray-drying of detergent compositions. It consists of injecting an inert gas, normally air, into the aqueous slurry, up to the saturation point, i.e. the point beyond which the physical stability of the slurry is disturbed. The incorporation of the phosphate esters employed in accordance with this invention reduces the density of the granules whether or not an inert gas is injected into the slurry, and the effect of air injection is additive. The above-mentioned carrier matrix from which a phosphate ester has been omitted typically has an approximate density of 600 grams/litre when produced by a spray-drying process wherein no gas injection is used, although the carrier matrix has an approximate density of 500 grams/litre when produced with gas injection and no phosphate ester addition.

To form a detergent composition, it remains for the present spray-dried carrier granules to be loaded with an organic nonionic detergent. A proportion of from 5% to 25%, preferably 10% to 20%, by weight, based on the total granule weight, of the desired nonionic detergent(s) may be sprayed on to the carrier granules by any applicable method.

Water-soluble organic nonionic detergents useful in connection with the present invention are typified by the compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted, to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic

elements.

For example, one well-known class of nonionic organic detergents is that available under the trade name "Pluronic". The compounds in question are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. Other suitable nonionic organic detergents include polyethylene oxide condensates derived from alkylphenols, e.g. condensation products of alkylphenols having an unbranched or branched alkyl group, containing (e.g.) 6 to 12 carbon atoms, with ethylene oxide, the ethylene oxide being attached in proportions of 5 to 25 moles of ethylene oxide per mole of alkylphenol.

The water-soluble condensation products derived from ethylene oxide and unbranched or branched aliphatic alcohols having from 8 to 22 carbon atoms, e.g. one derived from a coconut alcohol and ethylene oxide and having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol component having from 10 to 14 carbon atoms, are also useful nonionic detergents, and are in fact preferred herein.

Water-insoluble organic nonionic detergents, e.g. as described in Luxembourg Patent Specification No. 69,256, may also be used. These are detergents of the formula R_nOH wherein R represents an alkyl or alkenyl group having from 8 to 22 carbon atoms or an alkylated or alkenylated phenyl group having from 6 to 12 carbon atoms in the alkyl or alkenyl group, x is 2 or 3, and n is from 1 to 8. The hydrophilic-lipophilic balance (HLB) of these detergents, calculated according to Becker's "Emulsions Theory and Practice", Reinhold Publishing Co., pages 233 and 248, is less than 10.0.

Commonly used auxiliary components of detergent compositions can either be added to the aqueous slurry as described above, or be dry-mixed with the loaded carrier granules. Certain auxiliary components which would not withstand a spray-drying operation, e.g. sodium perborate, can instead be dry-mixed with the loaded carrier granules if required.

The following Examples illustrate the invention.

EXAMPLE I

An aqueous slurry of the following composition on a dry weight basis is formulated:

	% by wt.	
Sodium tripolyphosphate (STPP)	61.5	
Sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O} = 2.0$)	6.3	
Sodium sulfate	25.4	125
Phosphate ester*	0.36	
Sodium carboxymethylcellulose (CMC)	0.9	
Sodium ethylene diamine tetraacetate	0.3	
Miscellaneous	balance	
*The phosphate ester is a mixture of 80%		

ethoxylated monoalkyl acid phosphate and 20% ethoxylated dialkyl acid phosphate wherein each compound has 16 carbon atoms in its alkyl groups and an average of 2 ethylene oxide groups.

The slurry contains 45% water. Air is injected into the slurry prior to its being atomized into the top of a spray-drying tower. Hot air is introduced at the bottom of the tower and exits at the top. The resultant spray-dried granules contain 12% water and have a density of about 350 grams/liter. Granules produced under the same conditions except for the omission of the phosphate ester have a density of about 525 grams/liter.

A nonionic detergent (a 50:50 mixture of C_{14} and C_{15} alcohols ethoxylated with an average of 4 moles of ethylene oxide) is next sprayed onto the carrier granules to give loaded granules containing 18% nonionic detergent.

When used under typical washing conditions, the composition exhibited excellent cleaning performance, especially its ability to remove grease and oil stains.

EXAMPLE II

When Example I is repeated using mono-stearyl acid phosphate, monooleyl acid phosphate, monostearyl (EO)₁ acid phosphate, monostearyl (EO)₁₈ acid phosphate, monopropyl (EO)₃₀ acid phosphate, and distearyl acid phosphate at the same levels, substantially the same results are obtained.

EXAMPLE III

When Example I is repeated without an air injection step, the resultant spray-dried granules have a density of about 470 grams/liter.

EXAMPLE IV

Substitution of sodium carbonate for the sodium tripolyphosphate of Example I, gives substantially the same results.

EXAMPLE V

The effect that different levels of phosphate ester has on density is illustrated below. Example I is repeated using varying levels of the phosphate ester. The densities of the resultant granules follow:

Phosphate ester %	Density (grams/liter)
0	525
0.15	380
0.25	360
0.36	350
0.70	355
1.00	345

WHAT WE CLAIM IS:-

1. Carrier granules, as herein defined, having a bulk density of from 300 grams/litre to 500 grams/litre, the granules being produced by a spray-drying operation, being suitable for holding an organic nonionic detergent, and consisting essentially of (by weight):

(a) from 30% to 70% of a water-soluble alkaline inorganic builder salt;

(b) from 2% to 10% of an alkali metal silicate having a $SiO_2:M_2O$ ratio of from 3.2:1 to 1:1;

(c) from 10% to 50% of an alkali metal sulphate; and

(d) from 0.05% to 1.5% of one or more phosphate esters having the formula $(RO)_2(PO)(OX)$ wherein X is H, alkali metal, ammonium or substituted ammonium, and R is H or $R_1(OC_2H_4)_nOH$ wherein n is 0 to 30 and R_1 is an unbranched or branched alkyl or alkenyl group containing from 8 to 22 carbon atoms when n is 0 and containing from 2 to 22 carbon atoms when n is from 1 to 30, provided that no more than one R is H.

2. Granules as claimed in claim 1, containing from 0.25% to 0.6% (by weight) of the said phosphate ester(s).

3. Granules as claimed in claim 1 or 2, wherein, in the said phosphate ester(s), each R is $R_1(OC_2H_4)_nOH$ and n is from 1 to 30.

4. Granules as claimed in claim 3, wherein n is from 1 to 10 and R_1 contains from 12 to 16 carbon atoms.

5. Granules as claimed in claim 1, 2, 3 or 4, containing (by weight) from 40 to 65% of the alkaline inorganic builder salt, from 3 to 7% of the alkali metal silicate, and from 12% to 40% of the alkali metal sulphate.

6. Granules as claimed in any preceding claim, wherein the alkaline inorganic builder salt is sodium tripolyphosphate.

7. Granules as claimed in any preceding claim, having a bulk density of from 350 grams/litre to 450 grams/litre.

8. Granules as claimed in any preceding claim, but additionally containing from 5% to 25% (by weight, based on the total granule weight) of an organic nonionic detergent, which is incorporated in the granules after the spray drying step.

9. Granules as claimed in claim 1 or 8 having a composition substantially as indicated in any of the foregoing Examples.

10. A process for producing spray-dried carrier granules, as herein defined, having a bulk density of from 300 grams/litre to 500 grams/litre, comprising the steps of:

(i) forming an aqueous slurry consisting essentially of water together with ingredients "(a)", "(b)", "(c)" and "(d)" as specified in claim 1; and

(ii) spray-drying the slurry to form the carrier granules.

11. A process as claimed in claim 10 but additionally including the step of spraying, on to the spray-dried carrier granules, from 5% to 25% (by weight, based on the total weight) of an organic nonionic detergent.

12. A process as claimed in claim 10 or 11 wherein, in the said phosphate ester(s), each R is $R_1(OC_2H_4)_nOH$ and n is from 1 to

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30. 13. A process as claimed in claim 12 wherein n is from 1 to 10 and R_1 contains from 12 to 16 carbon atoms. 10
- 5 14. A process as claimed in claim 10, 11, 12, or 13 but additionally including the step of injecting an inert gas into the aqueous slurry before spray-drying. 15
15. A process as claimed in claim 10 or 11, substantially as described in any of the foregoing Examples. 10
16. Granules produced by a process as claimed in claim 10, 11, 12, 13, 14 or 15. 15
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